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6. AUTHOR(S)

Frank E. Karasz

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Univ of Massachusetts
Polymer Sciences & Engineering Room 701
Lederle Graduate Research Center
Box 34530
Amherst MA 01003-4530

8. PERFORMING ORGANIZATION REPORT NUMBER

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The underlying premise of the research is that organic polymer films 1-100 um in thickness composed of guest-host polymer materials or functional polymer materials exhibit useful optical, electro-optical or dielectric/electrical properties. Such films show promise as mdeial for optical data-storage and processing and non-linear optics (NLO). However practical device materials require the properties to be optimized and their function (e.g. NLO activity) should be retained in time. Improved performance of organic films may be achieved through molecular design and molecular engineering and an under-standing of the fundamental relationships between the macroscopic optical, electro-optical and dielectric properties and the molecular structure and molecular dynamics in the materials. To this end a major joint effort has been made for liquid crystalline side-chain (LCSC) polymers.

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FRANK E. KARASZ

DEPARTMENT OF POLYMER SCIENCE & ENGINEERING

UNIVERSITY OF MASSACHUSETTS

AMHERST, MA 01003

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DEPARTMENT OF POLYMER SCIENCE & ENGINEERING

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AMHERST, MA 01003

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CONTENTS

ACKNOWLEDGEMENT

I. **TITLE:** Functional Polymers and Guest-Host Polymer Blends for Optical and Electronic Applications: A Molecular Engineering Approach

II. **PRINCIPAL INVESTIGATOR:** Dr. Frank E. Karasz
Polymer Science & Engineering
University of Massachusetts
Amherst, Massachusetts 01003

III. **SUB-CONTRACTORS:** Dr. G. Attard
Department of Chemistry
The University
Southampton S09 5NH UK

Dr. N. Ogata (from 9/15/89)
Department of Chemistry
Sophia University
Chiyoda-ku
Tokyo, JAPAN

Dr. G. Williams
The University College of Swansea
Singleton Park
Swansea SA2 8PP UK

IV. **GRANT NUMBER:** F49620-87-C-0111
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V. **SENIOR RESEARCH PERSONNEL:** Dr. M. Nazemi
Dr. J. S. Dave
Dr. D. M. Rice
Dr. C. T. Imrie
Dr. J. S. Rutt
Dr. T. Schleeh
Dr. Emanuél Debeupte
Dr. Kanbai Wan
Dr. Kohei Sanui
Dr. Masahiro Rikukawa
Dr. Takashi Aoki
Dr. Tomoko Ueda

VI.   JUNIOR RESEARCH PERSONNEL: A. Wallington
S. Sproston
S. Yokoyama
H. Katagiri
Y. Kiyohara
Y. Takahashi

VII. ABSTRACT OF ACCOMPLISHMENTS

This report is for the period 15 September 1987 to 14 April 1993 and covers a multi-national research program in the area of multi-functional polymers for optical and electronic applications. From the inception the P.I. had the collaboration of two investigators in the U.K., Profs. G. Williams (Swansea) and G. Attard (Southampton). A fourth member of the consortium, Prof. N. Ogata (Tokyo) was funded as of September 15, 1989.

The underlying premise of the research is that organic polymer films 1-100 μm in thickness composed of guest-host polymer materials or functional polymer materials exhibit useful optical, electro-optical or dielectric/electrical properties. Such films show promise as media for optical data-storage and processing and non-linear optics (NLO). However practical device materials require the properties to be optimized and their function (e.g. NLO activity) should be retained in time. Improved performance of organic films may be achieved through molecular design and molecular engineering and an understanding of the fundamental relationships between the macroscopic optical, electro-optical and dielectric properties and the molecular structure and molecular dynamics in the materials. To this end a major joint effort has been made for liquid crystalline side-chain (LCSC) polymers. We have studied the alignment behavior of LCSC polymer materials in directing E-fields and their molecular dynamics, using dielectric relaxation spectroscopy (DRS) and optical microscopy. Broad-band DRS ($10-10^5$Hz) and optical microscopy and the electro-optical measurements were made using equipment developed during this grant.

Carbon-chain and siloxane-chain polymers having different potential applications included JSH, D6, S15 and S16 (see text), that are suitable for optical data-storage using a thermorecording method, JSD2 a photoactive polymer that is suitable for optical data-storage using angular-dependent photoselection in polarized laser light and the CNP and NLO polymers that are suitable for second harmonic generation. All practical applications of these materials require that they be pre-aligned as a monodomain (Homeotropic, H; Homogeneous, Hs; or Planar, P) through action of surface forces or by directing E-fields.

Various types of thin films having good dielectric properties and high thermal stabilities were also synthesized at air/water interfaces by a Langmuir-Blodgett (LB) method. Ultra-thin films of poly(benzothiazole) (PBT) containing thiophene were successfully obtained by this method. Copolymers of PBT containing both thiophene and phenylene moieties were obtained as thin films to investigate the effect of the thiophene moiety on optical properties. Additional highly polar groups were incorporated into the PBT containing thiophene in order to enhance activities of non-linear optical (NLO) properties. NLO activities of these PBT thin films were evaluated in terms of third harmonic generation (THG); χ_3 values increased with increasing contents of the thiophene moiety. Highly polar groups in the PBT structure greatly enhanced the NLO properties.

Also it was possible to prepare liquid-crystalline copolymers with attached non-mesogenic groups that possess differing functionalities, for example, photo-and thermochromic, photoconductive, or hyperpolarizable units. Many of the applications

for side-chain liquid-crystalline polymers require a relatively high glass transition temperature (T_g) largely because this property enhances the long-term stability of either the stored information or the non-centrosymmetric distribution of dipoles achieved by poling in χ_2 nonlinear optical devices. Polystyrene-based liquid crystal polymers have been shown to exhibit suitably high T_gs. We have prepared several series of random copolymers including some that have a polystyrene backbone and nitroazobenzene and pyrene side chains. This choice of side chains provides the required functionalities. The nitroazobenzene groups act as mesogenic units as well as endowing the polymer with electrooptic activity. The pyrene moiety is well known for its photoconducting properties, its ability to form charge-transfer complexes, and its non-linear optical and fluorescent behavior. The particular combination of photoconductivity with χ_2 electrooptic activity yields a further functionality, namely, photorefractivity. The synthesis and liquid-crystal properties of this novel and truly multifunctional copolymeric system are described, as well as those of several other related copolymers.

VIII. DESCRIPTION OF RESEARCH UNDERTAKEN

1. LIQUID CRYSTALLINE SIDE CHAIN POLYMERS (Williams)

Alignment Behaviour

A. Homeotropic (H), Planar (P) or Intermediately-aligned (I) LCSC polymer films were prepared in ITO sandwich cells by application of a directing ac E-field to a sample in its LC state or by cooling from the melt into the LC state in the presence of the field.

The conditions for obtaining H, P or I samples were determined from a knowledge of the temperature-dependent crossover frequency $f_c(T)$ for the change in sign of the dielectric anistropy $\Delta\varepsilon$ (two-frequency-addressing principle) and the phase behaviour of a material. $f_c(T)$ was determined experimentally from our dielectric studies of differently-aligned samples for each SCLC polymer.

H, P and I samples were prepared by prescribed thermal/electrical treatments of the polymer films. Quantitative reproducibility was achieved. The ability to align materials varied markedly with polymer structure, the strength and frequency of the E-field, and thermal treatment used. JSH, D6 and CNP polymers were readily aligned in the LC state to form H- and P-aligned films but readily disaligned when the field was removed for T>Tg, the polymer glass-transition temperature. JSD2, S15 and S16 could only be aligned to the H-condition, easily on cooling from the melt but with difficulty in the LC state. We had shown previously that siloxane-chain homopolymers having longitudinally-attached mesogenic groups could not be aligned in the LC state so the new work revealed that copolymerization (as in S15, S16, JSD)

or spacing-out the mesogenic groups (as in CNP) or inclusion of laterally-attached mesogens (as in D6) greatly facilitates E-field alignment in the LC state.

DRS provides a simple, direct and quantitative non-optical method for determining the degree of macroscopic alignment in the LCSC polymer films. Measurement of the frequency-dependent complex permittivity $\varepsilon(f)$ for a sample allows its director order parameter S_d to be determined using the relation derived previously by us

$$\varepsilon(f) = (1+2S_d)\varepsilon_\parallel(f)/3 + 2(1-S_d)\varepsilon_\perp(f)/3$$

where $(\varepsilon(f) = \varepsilon'(f) - i\varepsilon''(f)$ and where $\varepsilon_\parallel(f)$ and $\varepsilon_\perp(f)$ are the principal permittivities of the LC phase and are determined from measurements of the H- and P-aligned films, respectively. Measurements of real permittivity $\varepsilon'(f)$ or loss factor $\varepsilon''(f)$ allowed S_d to be determined for samples prepared by different electrical/thermal treatment and for samples undergoing alignment in time in an E-field or undergoing disalignment - through surface forces or chain forces. Thus DRS was used to obtain alignment/realignment data *in situ* that are unobtainable by spectroscopic or optical methods and that is an important feature of the work of the Grant.

Polymers that readily aligned in the LC state using E-fields, i.e. JSH, D6 and CNP, readily disaligned when the field was removed. Disalignment was due both to surface forces at the ITO electrodes and to release of strain in the chain backbones that had been induced when the mesophase was aligned in the E-field. Cooling an E-aligned sample to below its glass transition temperature T_g stopped the disalignment processes.

The kinetics of E-field induced alignment was determined in terms of dielectric values of $S_d(t)$ for several polymers and was found to conform to the Leslie-Ericksen continuum theory that involves both the reorientation of the LC director and flow of the LC phase as a homeotropic monodomain is formed. The kinetics of P→H transformations were studied in detail for JSH and CNP ($S_d(t)$ changes continuously from -0.5 to +1.0 as P→H). DRS data showed that H-alignment was achieved with S_d = 0.99., but those samples only became transparent to optical quality on further annealing in the E-field, demonstrating that flow alignment creates domain walls that scatter light and may only be removed by annealing in the E-field.

As a result of these fundamental studies it was shown that each polymer film could be aligned to a pre-determined state (H,P,I) in a quantitative manner and the extent of alignment could be determined, through S_d obtained from DRS measurements.

B. Molecular Dynamics

DRS studies of the SCLC polymers revealed complex relaxation processes that were dependent in a systematic way on the alignment condition of a film. Data for dielectric dispersion $\varepsilon'(f)$ and dielectric absorption $\varepsilon''(f)$ were obtained over wide ranges of frequency (f) and temperature for samples prepared in different states of macroscopic alignment. The dielectric relaxations arise from the anisotropic reorientational motions of dipolar mesogenic groups in the LC phase.

A theory of dielectric behaviour of LC polymers of the kind studied here was based on time-dependent statistical mechanics and showed that

$$\varepsilon_{\parallel}(f) = F(\mu_t, \mu_\iota, \mathfrak{I}(\Phi_{00}(t)), \mathfrak{I}(\Phi_{01}(t)))$$

$$\varepsilon_{\perp}(f) = f(\mu_t \mu_\iota, \mathfrak{I}(\Phi_{10}(t)), \mathfrak{I}(\Phi_{11}(t)))$$

where μ_t, μ_ι are component dipoles of the mesogenic group, $\mathfrak{I}$ indicates a Fourier transform and the $\Phi_{ij}(t)$ are the four orthogonal relaxation functions (time-correlation functions) for the motions of the mesogenic groups in the anisotropic LC potential. Using these results all the DRS data for all the polymers, in different states of alignment, could be fitted quantitatively. The prominent δ-process observed for H-aligned samples corresponded to the 00 mode, i.e. of $\Phi_{00}(t) = \langle\cos\beta(0).\cos\beta(t)\rangle$ for motion of μ_t with respect to the director axis **n**. Since the dielectric properties of LC materials determine the alignment behaviour in E-fields (through Δε), the understanding achieved at the molecular level for the DRS behaviour together with the Leslie-Erickson continuum theory of alignment provides a sound theoretical framework in which the alignment behaviour, and hence the electro-optical behaviour of these LCSC polymer films, is understood in some detail.

The stability of E-field-poled electret samples of LCSC polymers was investigated using the thermally-stimulated depolarization current method. The changes in the TSCD curves obtained when freshly-prepared poled films were aged for different times and at different temperatures in the glassy LC state gave quantitative data for loss of polarization through ageing, and hence a prediction of the loss of property (e.g. NLO SHG coefficients) with time. Our data suggest that facile motions in the glassy LCSC polymer percolate through the sample and remove the perturbation of the distribution function for dipole orientation that had been

produced on cooling the polymer in a directing dc field into a glassy LC state. Our data make it clear that if secondary (β) relaxations can be minimized through chemical design then this ageing process would not take place so that the stored electric polarization, and hence NLO coefficients, would not decay away in time.

C. Theoretical Aspects of Dielectric Relaxation

The multiple dielectric relaxation processes that occur in amorphous, crystalline and LC polymer materials play an important role in determining their optical electro-optical and dielectric/electrical properties. In parallel studies to the Grant work we have made experimental DRS studies of NLO dye/host-polymer materials that may be used for SHG applications [see Dionisio, Moura-Ramos and Williams, "Molecular motions in Poly(vinyl acetate) and Poly(vinyl acetate)/p-nitro-aniline mixtures", Polymer, $\underline{34}$, 4105-4110 (1993) and "Dipolar relaxation behaviour in PMMA/4-nitroaniline solid solutions, Polym. Intern. $\underline{32}$, 145-151 (1993)]. The motions of guest dye with host polymer are complex and involve coupled $\alpha\beta$ processes in the amorphous glass or rubbery material. As part of this Grant we have examined the theory of multiple dielectric relaxation for amorphous, crystalline and LC polymers. We show how multiple dielectric processes (α, β, $\alpha\beta$) in amorphous polymers arise from angular motions of dipoles and how $\varepsilon(f)$ may be related to molecular time-correlation functions of those motions, leading to an understanding of the coupling between α, β and $\alpha\beta$ processes. The observation that α and $\alpha\beta$ dielectric processes in amorphous are well-approximated by the Kohlrausch-Williams-Watts function is rationalized in terms of different possible mechanisms for motion.
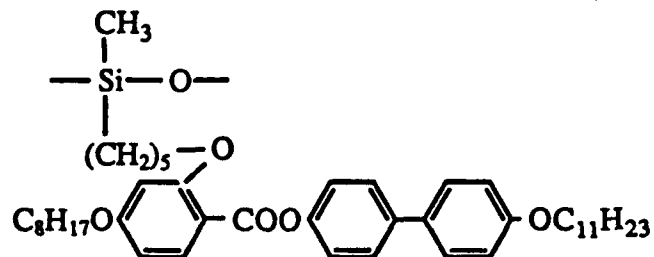
A critical examination of the physical bases of memory-function and recent mode-mode coupling theories of dielectric relaxation has been made.
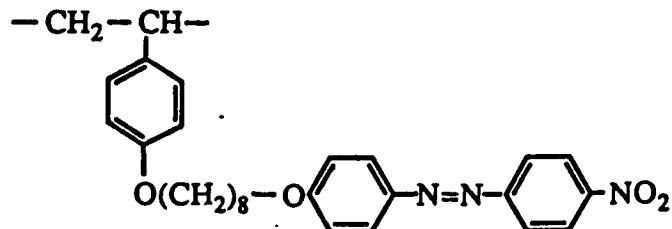
Materials

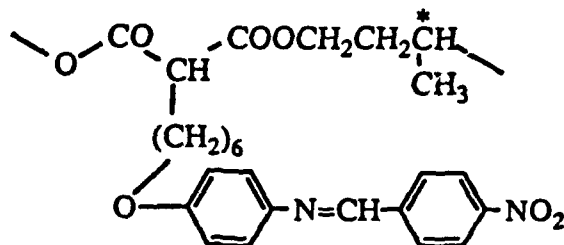1. **Copolymer with longitudinal and transverse LC groups, JSH.** T_g 6°C; T_c 120°C. (Gray and Lacey).
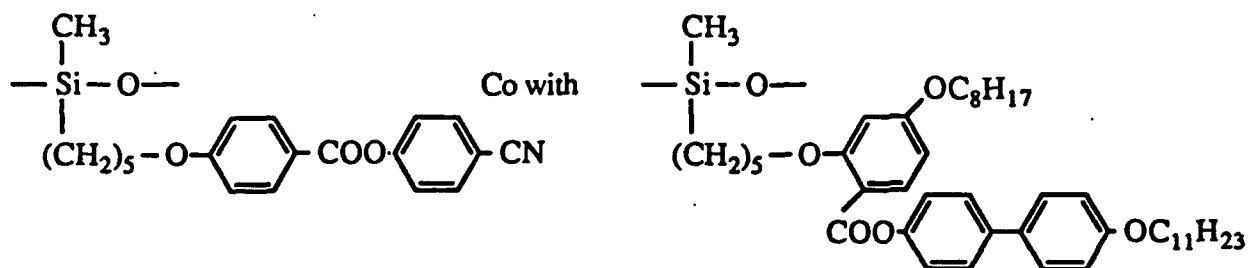
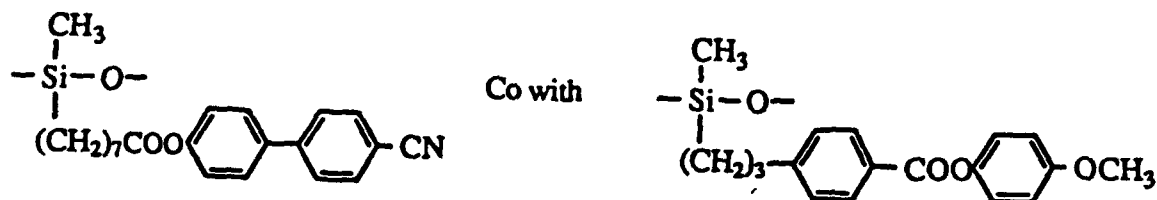2. **Polymer with transverse LC group, D6.** T_g 9°C; T_c 61°C. (Gray and Lacey).

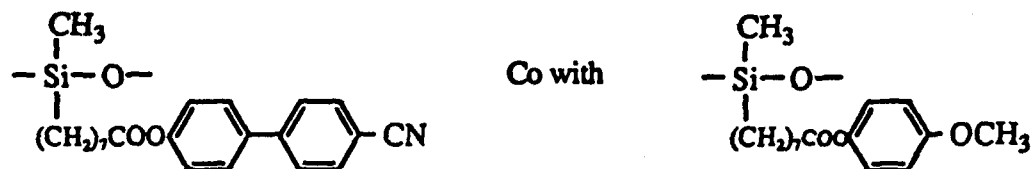3. **Photoactive polymer, JSD2.** T_g 55°C; T_c 110°C. (Attard).

4. **Chiral-nematic NLO polymer, CNP.** T_g 5°C; T_c 51°C. (Griffin).

5. **50:50 Copolymer with mixed mesogenic groups, S16.** T_g 16°C; T_c 117°C. (Matsumoto).

6. **50:50 Copolymer with mixed mesogenic groups, S15.** T_g -6°C; T_c 74°C. (Matsumoto).

2. THIN FILMS OF DIELECTRIC POLYMERS FOR OPTICAL APPLICATIONS

(Ogata)

High temperature polymers such as poly(benzimidazole) (PBI), poly(benzoxazole) (PBO) or poly(benzothiazole) PBT) are highly stable at elevated temperatures above 300°C and have the fully extended structures of conjugated systems. Therefore their non-linear optical (NLO) properties have been studied in terms of second and third harmonic generations. Particularly, PBT is known to have a relatively high NLO activity.

However, these high temperature polymers are infusible and insoluble in common organic solvents and processing to form thin films is rather difficult. It was reported by my group that thin films of these high temperature polymers such as PBI, PBO or PBT were successfully obtained at air/water interface by using a Langmuir-Blodgett (LB) method and their NLO properties were investigated.

It is expected that a higher electron density in PBT structure would enhance the NLO properties. Therefore, PBT containing a thiophene moiety in main chains was prepared as thin films by using the same method at air/water interface as reported previously. Additional highly polar groups in PBT also may enhance the NLO properties. Therefore a dioxyethylene group was incorporated into thiophene and a thin film of highly dielectric PBT containing the modified thiophene was synthesized.

NLO properties of these thin films of PBT derivatives were evaluated in terms of second (SHG) and third harmonic generations (THG).

a) Synthesis of SHG active PBT

SHG active PBT was obtained at air/water interface as described schematically in Fig. 1, by incorporating electron-accepting nitro group in PBT:
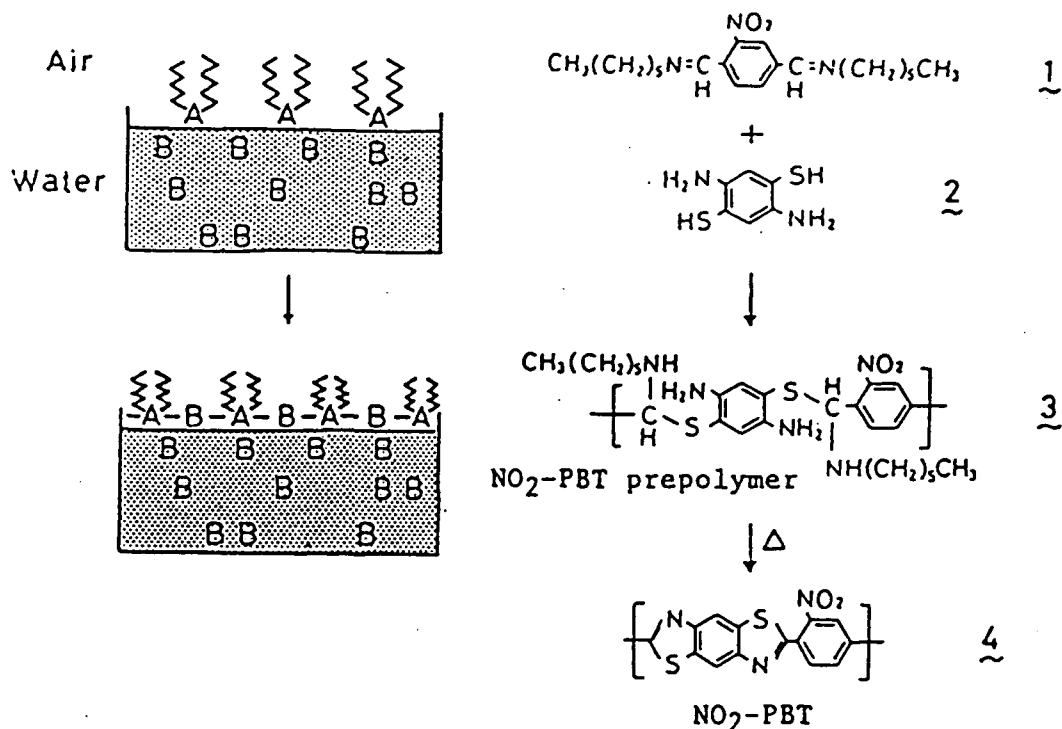
The SHG intensity of the NO_2-PBT prepolymer was evaluated as $\chi_2 = 21$ pm/V. However the SHG intensity decreased remarkably with increasing heat-treatment temperatures to prepare NO_2-PBT, as shown in Fig. 2, in which the SHG intensities were compared with the absorption peak ratios between CH_2 and NO_2, which represented the structural change from the prepolymer to NO_2.
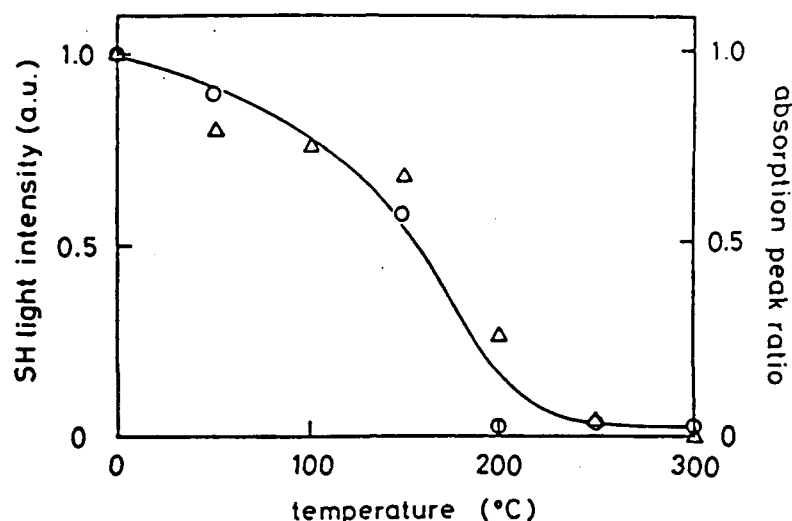
The decrease in the SHG light intensity might be due to the randomization of the well-ordered structure of the NO_2-PBT prepolymer which might be caused by the heat-treatment at high temperatures. In order to improve the SHG intensity, corona poling method was applied to the thin film of NO_2-PBT after the heat-treatment. Conditions for the corona poling was as follows: distance from cathode = 1 cm, voltage = 9 kV, temperature = 110°C, time = 1 hr. Fig. 3 indicates the SHG intensity of the poled NO_2-PBT in comparison with the NO_2-PBT after the heat-treatment at 300°C for 30 min.
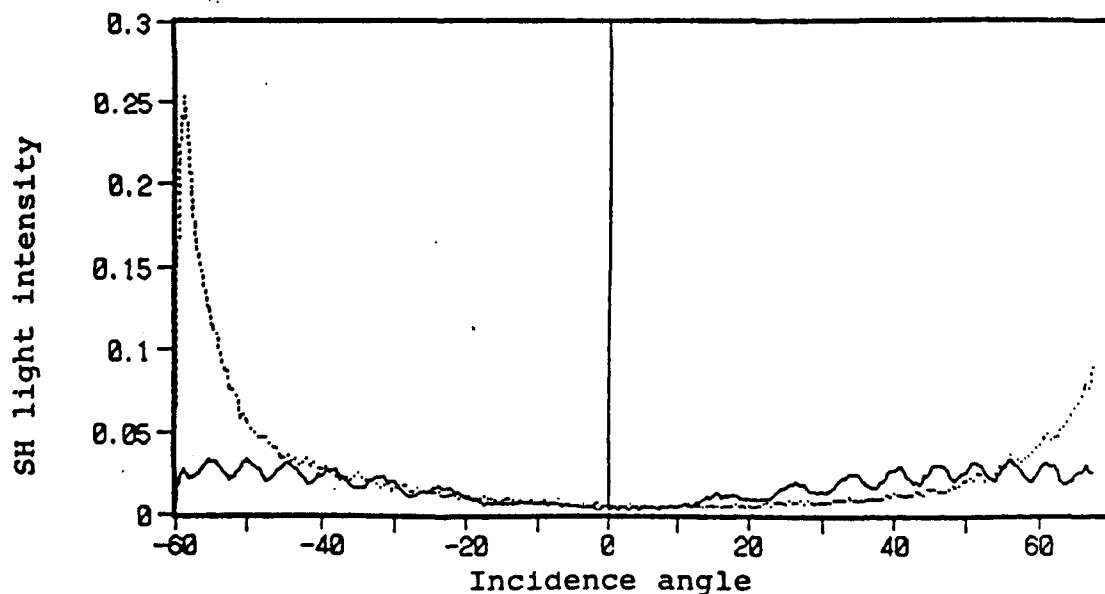
It is seen in Fig. 3 that the SHG intensity increased by the corona poling method and the χ_2 value was evaluated as 25 pm/V. The relaxation behavior of the SHG intensity of the poled NO_2-PBT was very stable and no change of the SH light intensity was observed after one month at room temperature. Perhaps the rigid structure of NO_2-PBT prevents the relaxation, as was expected before. This result was a notable achievement for the novel type NLO polymers.

b) Synthesis of THG active PBT

(1) Thiophene-containing PBT

It was expected that the incorporation of electron-donating groups such as thiophene might enhance χ_3 value of PBT thin films because of the more polar character of the backbone of PBT. The χ_3 values for the PBT precursor polymer, and the PBT containing thiophene were of the order of 10^{-11} esu which are higher than PBT itself.

It was previously found that fabrication of poly(benzothiazole) (PBT) as a uniform thin film can be accomplished by using the LB method at air/water interfaces. The NLO properties were evaluated by means of second harmonic generation (SHG) measurements. Higher order, third harmonic generation(THG) outputs, may be obtained when electron-donating groups are incorporated into the PBT structure. Therefore, PBT containing a thiophene moiety was designed to produce THG active thin films by using the LB method.

The thiophene PBT compound was prepared at the air/water interface

by the following reaction scheme through the process as shown in Fig. 4:

Monomer A

Monomer B

PTBT prepolymer {A-B}
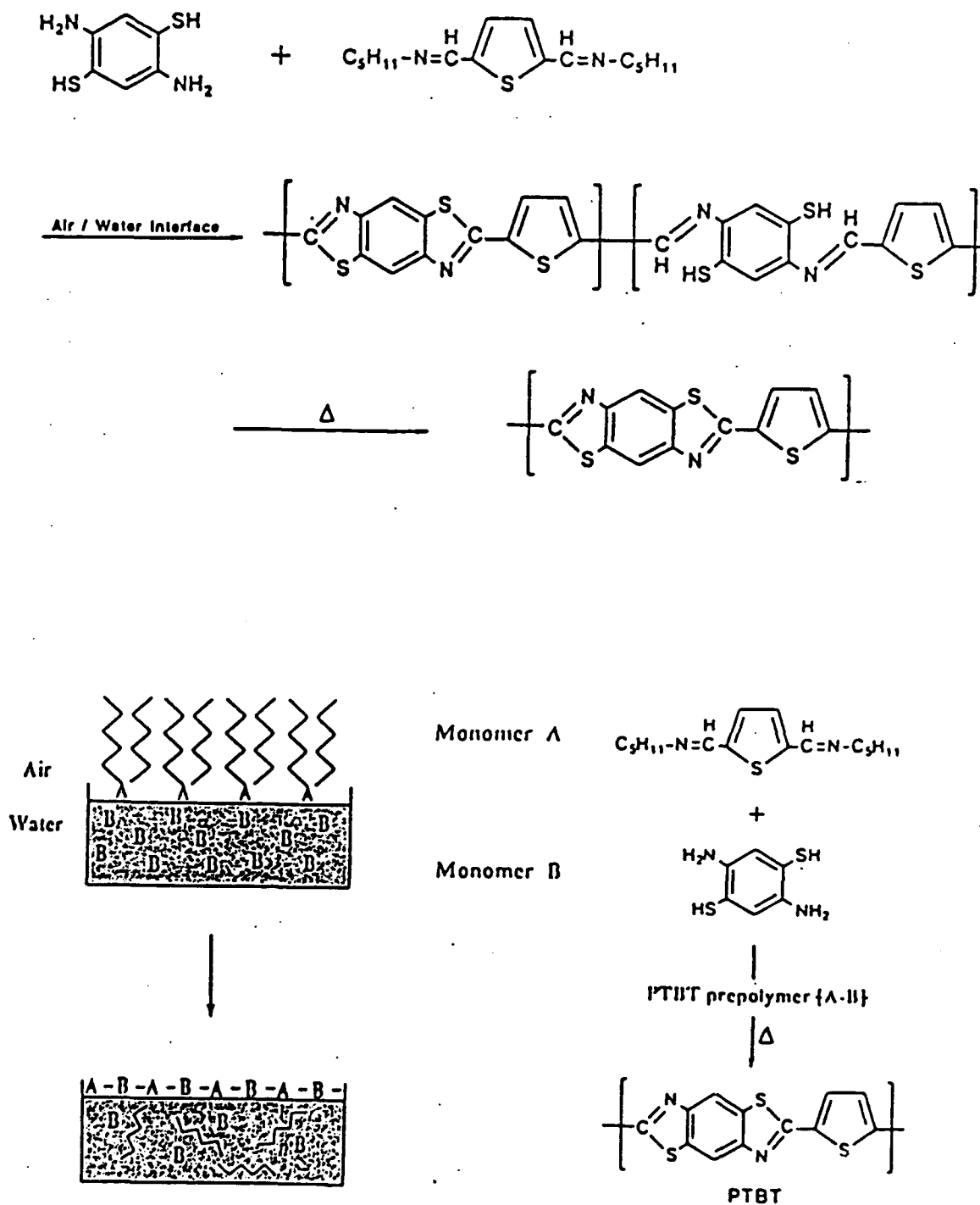
PTBT

Thin films of PTBT were obtained as follows: 2,5-thiophenedipentylaldimine was spread on water surface as a monolayer film in a LB trough, in which 2,5-diamino-1,4-benzenedithiol was dissolved in the aqueous phase. The reaction proceeded at room temperature for 24 hours and the thin film formed at air/water interface was transferred onto a quartz plate by a horizontal lifting method.

Electronic spectra of the thin films are shown in Fig. 5 as a function of number of layers and it is seen that absorptions at 420 nm increased linearly with increasing the number of layers of the built-up films, indicating that uniform thin films were formed by the LB method. One layer thickness of the built-up film of PTBT was about 35 Å.
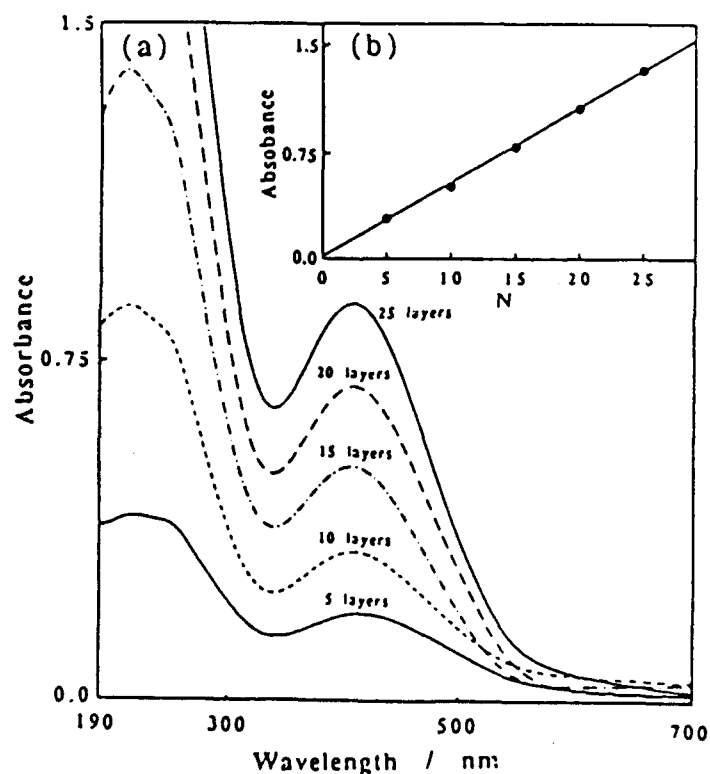
Third harmonic generation of the built-up films of PTBT was measured and χ_3 values of these built-up films were calculated as shown in Table 1.

Table 1. χ_3 measurements of thin films of PTBT as a function of curing temperature

Sample (20 layers)	$\chi_3(10^{-11}esu)$
As made	1.3
120°C	1.6
180°C	1.9
200°C	2.6
240°C	2.4

χ_3 values of the heat-treated film at 200°C reached 2.6×10^{-11} esu, which was almost twice as high as that of the as-made film. This value is almost 5 times higher than that of PBT containing only phenylene group.

(2) PBT containing both thiophene and phenylene groups

Copolymers of PBT containing both thiophene and phenylene units were prepared by the same method at air/water interface,by changing molar ratios between aldimines containing thiophene and phenylene units, as shown below:
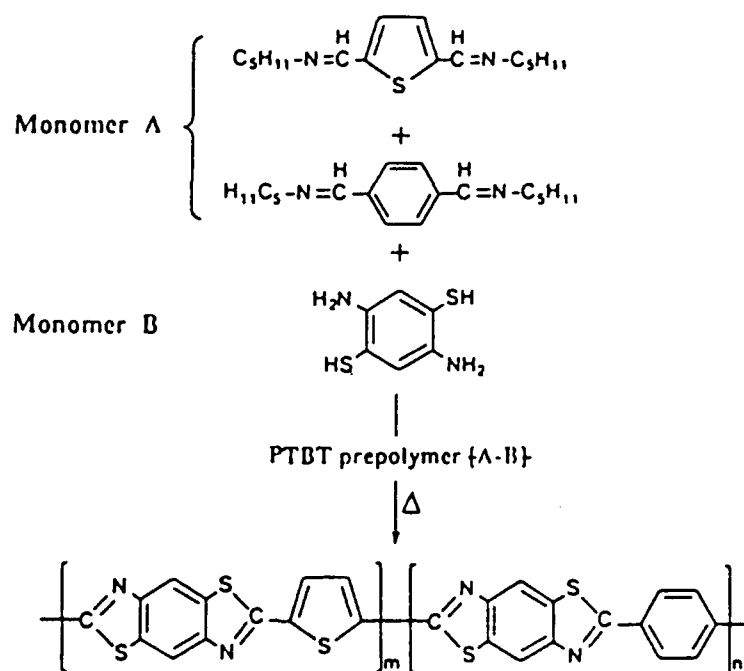
Thin films of PTBT containing thiophene and phenylene groups were prepared by the LB method and their third harmonic generations were evaluated, as shown in Fig. 6. It is clearly seen in Fig. 6 that χ_3 values increase with increasing contents of thiophene moiety in the copolymers.
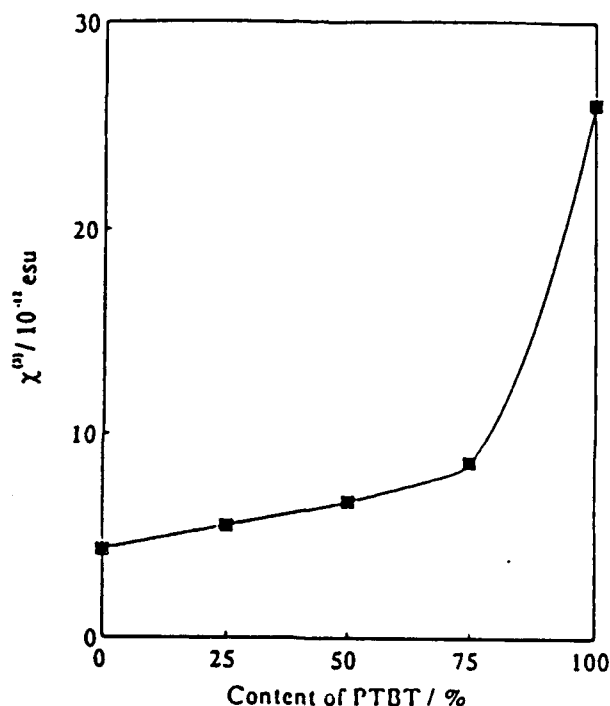
Enhancement of third harmonic generation of PTBT containing thiophene might be ascribed to the high electron-donating property of the thiophene moiety. These results may lead to another molecular design for higher THG activities.

(3) PBT having highly polar groups on thiophene

It was previously found that poly(benzothiazole) incorporating thiophene(thiophene-PBT) could be fabricated as a uniform thin film at an

air/water interface using the LB method. The thin film of thiophene-PBT exhibited enhanced non-linear optical properties as measured by third harmonic generation (THG) and the χ_3 values of the thin film was five times higher than that of PBT not incorporating the thiophene moiety.

The enhancement of the NLO properties resulted from the more polar structure of the PBT with the thiophene moiety incorporated into the main chains. Therefore, it was expected that additional polar groups in the thiophene might further enhance the NLO properties of the polymer. Based on this expectation, the highly polar thiophene dicarboxylic acid shown below was synthesized by the reactions:
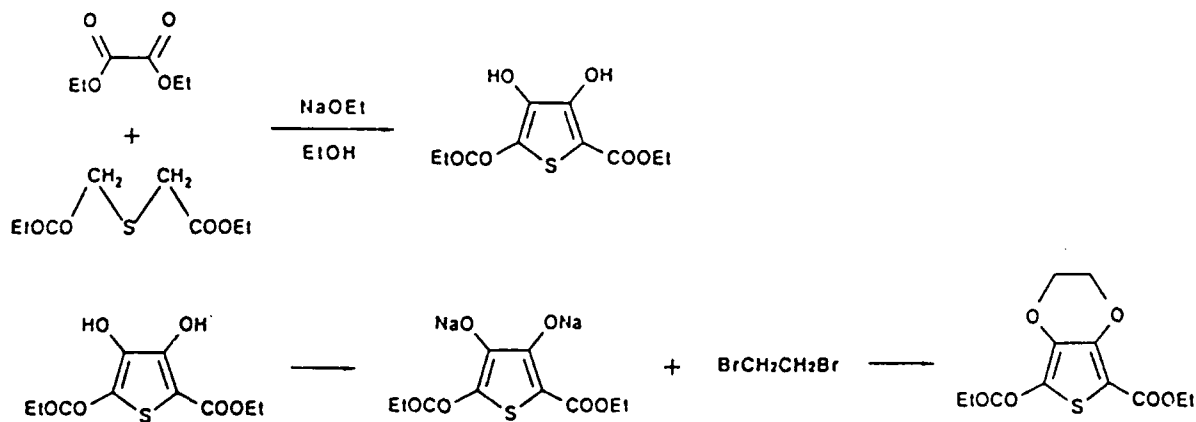
The 3,5-Dioxyethylene-2,5-thiophenedicarboxylic acid was then converted to the corresponding aldimine derivatives which were reacted with 2,5-diamino-1,4-dithiol benzene at the air/water interface to form thin films of a

polar thiophene-PBT as shown below:

Monomer A

+

Monomer B
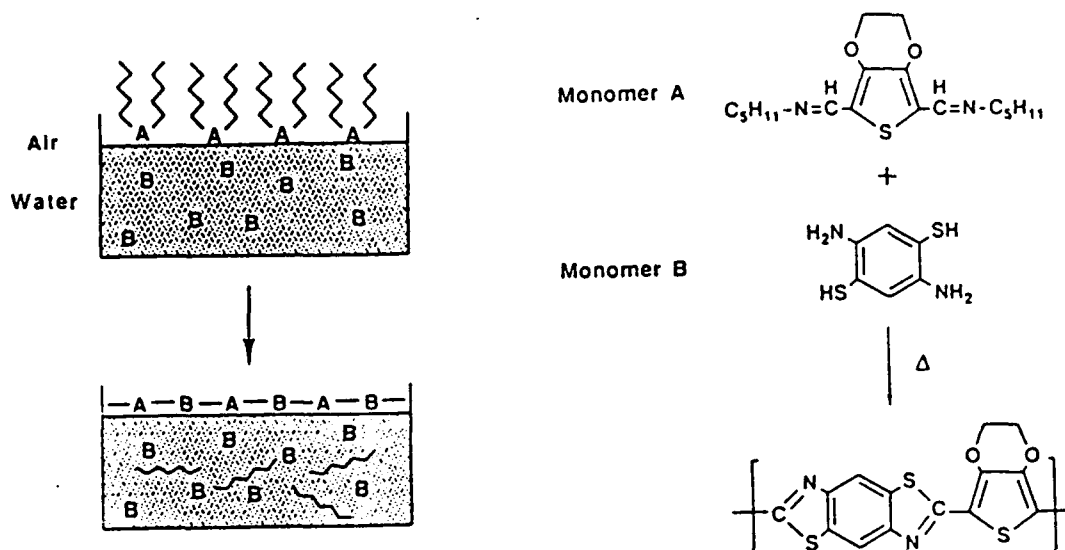
Optical properties of the DOT-PBT thin film were evaluated as follows:

REFRACTIVE INDEX   = 1.85 at 450 nm

χ_3 VALUE   = 2×10^{-10} esu

The THG results for these thin films yielded a value of $\chi_3 = 2 \times 10^{-10}$ esu, some ten times higher than that of homopolymer PBT. Thus, the effect of highly polar group on PBT on the enhancement of NLO properties was confirmed.

Various types of PBT having electron-accepting and -donating groups were synthesized at air/water interface by the LB method to obtain thin films and their NLO properties were evaluated. PBT having nitro group exhibited the SHG activity and PBT containing electron-donating thiophene group

showed a high THG activity in comparison with conventional PBT.

3. <u>ULTRASTRUCTURE STUDIES OF SIDE-CHAIN LIQUID-CRYSTALLINE COPOLYMERS</u> (Attard, Karasz)

At the root of LC application potential is the duality of properties exhibited by these polymers combining the characteristics of macromolecules, e.g., glassy behavior and processibility, with the electrooptic properties of low-molar-mass mesogens. A critical stage in the processing of these polymers for use in information storage or nonlinear optics is the director alignment of the mesophase in an electric field. The alignment requires that the mesogenic units have a positive dielectric anistropy ($\Delta\epsilon$), as provided by, e.g., a nitroazobenzene group. It is well known, however, that groups with a strong permanent dipole moment tend to form antiparallel correlations in a condensed phase including mesophases, and this behavior reduces the effective $\Delta\epsilon$ of the system. In devices using low-molar-mass mesogens this problem was solved by using mixtures of compounds with high and low values of $\Delta\epsilon$ in which the nonpolar compounds serve to disrupt the formation of the antiparallel dimers. A disadvantage of this approach is that such mixtures, in which the constituents may exhibit only nematic phases, tend to exhibit induced smectic phases. This result has been interpreted in terms of a specific interaction, often assumed to be charge transfer, between the unlike mesogenic cores. We have shown recently that such interactions can also affect the properties of side-chain liquid-crystalline copolymers containing potential charge transfer

groups of high and low $\Delta\varepsilon$. To investigate further the role of specific interactions in determining transitional properties and as part of a continuing program to develop new materials for electrooptic applications, we have prepared new copolymer systems based on atactic polystyrenes.

The polystyrene backbone was chosen because this structure endows the derivative polymers with relatively high glass transition temperatures, an important consideration in the development of materials suited to information storage or nonlinear optics. The nitroazobenzene is a prototypical group of interest in nonlinear optic applications, and both azo-containing units are photochromic and suited to information storage technologies.

The synthetic route taken to prepare to copolymers in shown in Scheme 1. The proposed molecular structures for the polymers were verified by ^{1}H-NMR spectroscopy, by IR spectroscopy and by elemental analyses.

The poly(4-hydroxystyrene) used in this study yields derivatized copolymers with a degree of polymerization (DP) of ca. 80. A recent investigation in which cyanoazobenzene or cyanobiphenyl were used as mesogens suggests that polymers with this DP may still lie in the regime in which transitional properties show molecular weight dependence. To develop a texture that enabled us to identify the mesophasic type, we cooled the copolymers from a temperature at least 10°C above their clearing points. At the transition, bâtonnets developed and coalesced to yield a focal-conic fan texture, an arrangement implying a layered structure. In addition, several
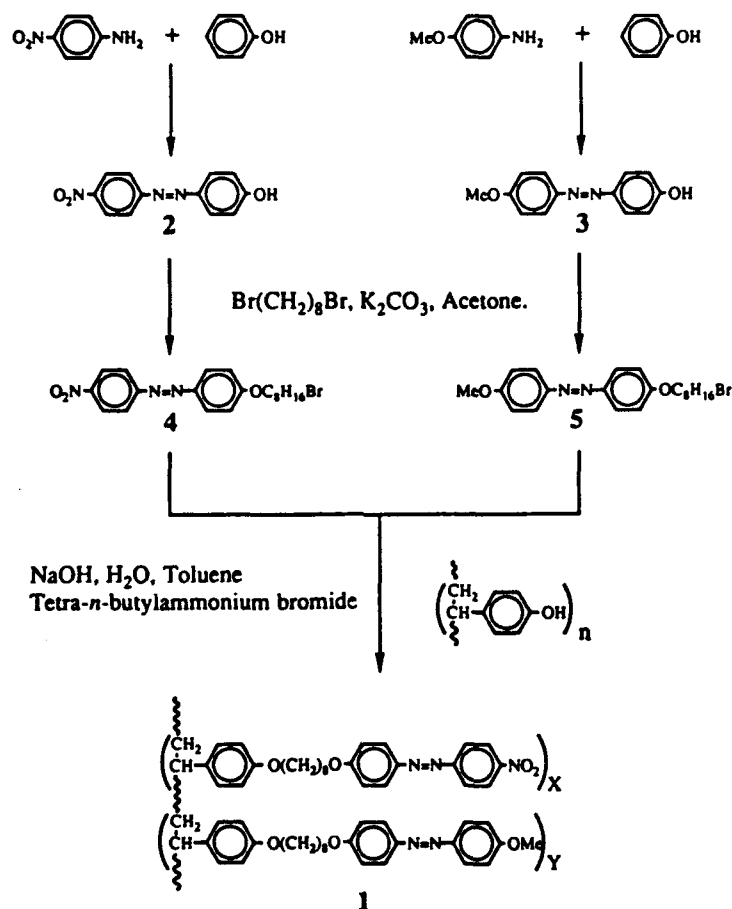
Scheme 1.

preparations contained regions of homeotropic alignment, a result implying an orthogonal arrangement of the director with respect to the layer planes. The mesophase exhibited by these copolymers therefore is assigned as a smectic A phase. This assignment was confirmed using x-ray diffraction.

The entropies measured for the smectic-isotropic transition suggest differences in the structure of the smectic A phases exhibited by these copolymers. To investigate this possibility, we examined the layer spacings. Various structural modifications of the smectic A phase may be distinguished,

in general, by using the ratio of the measured layer spacing, d, to the all-trans molecular length, l. For example, the conventional smectic A phase, denoted S_{A1}, has a d/l ratio approaching unity, whereas the bilayer S_{A2} phase has a d/l ratio of ca. 2. Between these two extremes lie a series of interdigitated smectic A phases for which $l<d<2l$. For low-molar-mass mesogens, it is often straightforward to calculate the d/l ratio and to assign the phase on this basis. For side-chain polymers, this is not the case, because of ambiguity in the definition of the all-trans molecular length, l. There exist two ways in which to define l for side-chain polymers: l_A may considered to refer to side chain itself, excluding the segment of the backbone to which it is attached; alternatively, the backbone (in this instance, the methylene group and phenyl ring) is included in the calculation of l_B. This ambiguity arises from the two possible arrangements of the polymer backbone within the mesophase. For the case in which the smectic field is strong enough to constrain the backbone to lie in the plane between the smectic layers, the backbone should be included in the estimation of l. However, if the smectic field has little effect on the backbone and consequently the latter is located in essentially an isotropic conformation, then we need not consider the backbone in calculating l. For polystyrene-based polymers, the two resulting values of l are very different. For the two homopolymers, the degree of overlap of the side chains in the smectic phase is also very different. For the methoxy-substituted homopolymer, d/l is 1.32 when the backbone is excluded and decreases to 0.99

when including the backbone. The corresponding values for the nitro-substituted homopolymer are 1.60 and 1.25, respectively. Using these values to construct a possible mean local arrangement of the side chains, we arrive at two structures. It is thought that the phase structure for mesogens possessing strong terminal dipoles is, to a large extent, governed by the formation of antiparallel dimers that serve to minimize the dipolar energy. It is difficult to propose an interaction that would be responsible for the high degree of overlap. This conclusion implies that the smectic field does not confine the backbone between the smectic layers but instead the repeat units of the styrene backbone have an essentially isotropic distribution of orientations. It is clear, irrespective of which arrangement is considered, that the methoxy side chains overlap to a greater extent than do the nitro side chains, and thus there is a greater interaction between the methoxyazobenzene unit and the spacer. This interaction is entropically unfavorable because it acts to order the spacer. The origin of the extra entropy, therefore, can be accounted for by the increased conformational change at the clearing point resulting from the interaction of the methoxyazobenzene moiety with the spacer.

It should be stressed that the ^{13}C-NMR spectra revealed that the spacer chain in these polymers does not exist exclusively in all-*trans* conformation but instead contains *gauche* defects. The presence of *gauche* defects in the mesophase is well documented and is in agreement with theoretical predictions

based on the rotational isomeric state model. The *gauche* defects have the effect of reducing the effective thickness of the smectic layers and, in principle, allow for antiparallel dimers in a structure that confines the backbone to lie between the layers. To remove this ambiguity regarding the role of the backbone in smectic phase formation, we used the relative intensities of the Bragg reflections to construct the electron density profile of the layer.

Thus we conclude that the transitional properties of copolymers containing mesogenic units of high and low dielectric dispersion show a nonlinear dependence on composition. This strongly resembles the behavior of low-molar mass mesogenic systems that has been attributed to a specific interaction between the unlike cores. Such an explanation also accounts for the present observations. Side-chain liquid-crystal polymers and copolymers of several other structures were synthesized and studied in this research program. Details are given in the publications listed below.

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